Progress in High Stability Amorphous Silicon-Based Solar Cells with Guidance from Real Time Optics*

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ABSTRACT

The preparation and optimization of high performance, high stability amorphous silicon-based thin films and solar cells has been guided by insights obtained from real time optical studies. An important concept in establishing guiding principles is the deposition phase diagram. The phase diagram in its most advanced form describes the values of a key deposition variable (such as the H_2-dilution ratio R) and the accumulated bulk layer thickness d_b at which different microstructural transitions are detected for a given substrate material. Such transitions include (i) an amorphous roughening transition [a→a] (in which case the film remains amorphous on both sides of the transition), (ii) an amorphous - to - (mixed-phase amorphous + microcrystalline) roughening transition [a→(a+μc)], and (iii) a (mixed-phase) -to-(single-phase microcrystalline) smoothening transition [(a+μc)→μc]. In general for a given substrate material, i-layers in solar cells optimized for the key deposition variable are obtained just prior to the a→(a+μc) transition, such that the Si:H film remains amorphous throughout deposition to the desired thickness. We have described such films as "protocrystalline", implying that if the deposition was continued, then a mixed-phase (a+μc)-Si:H film microstructure would evolve.

1. Introduction: Overview of Previous Research

In our previous research efforts, real time spectroscopic ellipsometry (RTSE) has been applied to establish guiding principles for fabrication of high performance, high stability amorphous silicon (a-Si:H) based p-i-n solar cells by rf plasma-enhanced chemical vapor deposition (PECVD). The first studies have provided a strategy for the optimization of amorphous silicon-carbon alloys as i-layers of p-i-n solar cells. In this strategy the H_2-dilution gas flow ratio, expressed by $R=[H_2]/\{[SiH_4]+[CH_4]\}$, should be maintained at the highest possible value while avoiding a transition to the microcrystalline film growth regime at high R [1]. Subsequent research on unalloyed a-Si:H emphasized the fact that the amorphous-to-microcrystalline transition is dependent on the substrate and on the accumulated thickness [2,3]. As a result, the optimized conditions for i-layer fabrication depend on the chosen solar cell structure and on the desired i-layer thickness. To illustrate these points, simple deposition phase diagrams have been developed by RTSE for a-Si:H i-layers [4]. For a given substrate, these diagrams plot the accumulated thickness at which the [a→(a+μc)] transition occurs as a function of the deposition variable $R=[H_2]/[SiH_4]$. The simple phase diagrams have shown that, in an optimum two step i-layer process, the H_2-dilution ratio R should be maintained at its highest possible value while ensuring that the a→(a+μc) phase boundary is not crossed *as the i-layer accumulates.*

2. Introduction: Overview of Recent Research

Our more recent studies have taken three directions.

First, we have extended the previous simple phase diagram concept for applicability in studies of higher rate a-Si:H i-layer growth. As a result, we include an observed amorphous-to-amorphous roughening transition [a→a] in addition to the amorphous-to-(mixed-phase microcrystalline) transition [a→(a+μc)]. Results so far suggest that the highest performance, highest stability materials not only require operation near the a→(a+μc) boundary but also require an a→a roughening transition at the largest possible thickness. For a-Si:H i-layers, such a situation occurs for R=10 at the lowest rf plasma power (rate: 0.5 Å/s), and under these conditions the film surface is stable throughout growth, with the a→a transition occurring above 4000 Å. Increases in rate toward 5 Å/s, obtained simply by increasing the plasma power, shift the a→a roughening transition to much lower i-layer thicknesses, an effect that correlates with rapidly deteriorating solar cell performance.

Second, we have explored multi-step i-layer processes in p-i-n solar cell fabrication that, along with solar cell modeling, have provided insights into the various difficulties encountered in this effort. Detrimental effects on solar cell performance may result from (i) a large discontinuity in mobility gap (~0.7 eV downward) within the i-layer due to an inadvertent a→(a+μc) phase transition, or even (ii) several smaller discontinuities (~0.1 eV upward and downward) due to changes in H_2-dilution ratio R designed to suppress the development of microcrystallites as the a-Si:H i-layer accumulates.

Finally, recent progress is also being made in adapting phase diagram concepts for optimization of the n-i-p a-Si:H solar cell configuration, and in particular for determining the optimum phase of the p-layer in this configuration. Our latest results suggest that optimum single-step p-layers are obtained in the protocrystalline regime, as well, just prior to the onset of microcrystallinity.

3. Recent Results: Higher Rate Si:H Deposition

As an example of our recent research efforts outlined above, we present a comparison of phase diagrams for Si:H film growth on crystalline silicon substrates under different conditions of rf PECVD. The goal of such studies is to elevate a-Si:H i-layer growth rates while retaining high performance and high stability in a-Si:H p-i-n and n-i-p solar cells. Figures 1 and 2 provide comparisons between pairs of superimposed phase diagrams for three series of Si:H film depositions. In each figure, the two important transitions are depicted for the superimposed phase diagrams: the a→a transition and the a→(a+μc) transition.

The deposition conditions for the two series in Fig. 1, are identical except for the rf plasma power. For the first deposition series (circles), the rf power is set at its minimum value for a sustainable plasma, 0.08 W/cm^2, leading to a deposition rate of 0.5 Å/s at the optimum H_2-dilution of

R=10. For the second deposition series (squares), the power was increased by a factor of ten to 0.8 W/cm^2, leading to a deposition rate of 3.5 Å/s at R=10. Fixed deposition parameters include the partial pressure of SiH_4 which was set at ~0.05 Torr (total pressures from ~ 0.05 Torr at R=0 to ~1 Torr at R=40) and a substrate temperature of 200°C. The effects of increased plasma power in Fig. 1 are clear. First, at lower R (0≤R≤10) the a→a transition is shifted to smaller thickness by an order of magnitude or more. Second, at higher R (20≤R≤40) the a→(a+μc) transition is shifted to larger thickness.

In Fig. 2, the phase transitions for the highest power (0.8 W/cm^2) deposition series (squares) are compared with the transitions for a third deposition series (circles) also at an elevated power (0.34 W/cm^2), but with a much higher total gas pressure of 4 Torr (fixed). In spite of the differences in plasma power for the two series in Fig. 2, the deposition rates are nearly the same, ~3.5 Å/s at the a→(a+μc) boundary (occurring at R=10 and 60, for the low and high pressure series, respectively). The increase in pressure leads to substantial changes in the phase diagram, in particular, a significant shift in the a→(a+μc) transition to much higher R. As a result, a wide window in R (20-60) opens within which the a→a transition occurs at relatively large thicknesses (>1000 Å).

4. Discussion: Higher Rate Si:H Deposition

In Fig. 1 at the low plasma power, a narrow window in R near R=10 is evidenced, within which a smooth, stable surface is retained throughout deposition of a relatively thick i-layer. Under these conditions, the a→a roughening transition occurs at a thickness >4000 Å for R just prior to the a→(a+μc) transition. This behavior, namely growth with a stable surface just within the amorphous side of the a→(a+μc) transition, is characteristic of i-layer deposition optimized for high performance and high stability of solar cells. The approach is likely to be associated with a number of desirable plasma and surface characteristics such as: (i) film growth predominantly from SiH_3 radicals with minimum contributions from SiH_n (n≤2) and higher silanes, (ii) low ion bombardment of the surface, (iii) effective hydrogenation of the surface for a long adsorbed SiH_3 radical diffusion length, and (iv) effective sub-surface relaxation of strained Si-Si bonds by H in-diffusion.

When the plasma power is increased under the lower pressure plasma conditions, the narrow window of optimum deposition closes due to the loss of one or more of these desirable plasma and surface characteristics. At higher pressures, the a→(a+μc) shifts to higher R possibly due to the increased probability of a reaction of atomic hydrogen with SiH_4 before the H reaches the film surface. It is this shift that reopens a broad window in R where the a→a transition occurs at relatively large thicknesses. Under these high power, high pressure conditions, SiH_4 depletion may be beneficial since it reduces the concentration of higher silane radicals reaching the film surface. In addition, ion bombardment is reduced as well. Thus, such an approach appears to be promising for higher rate rf PECVD of i-layers for solar cells.

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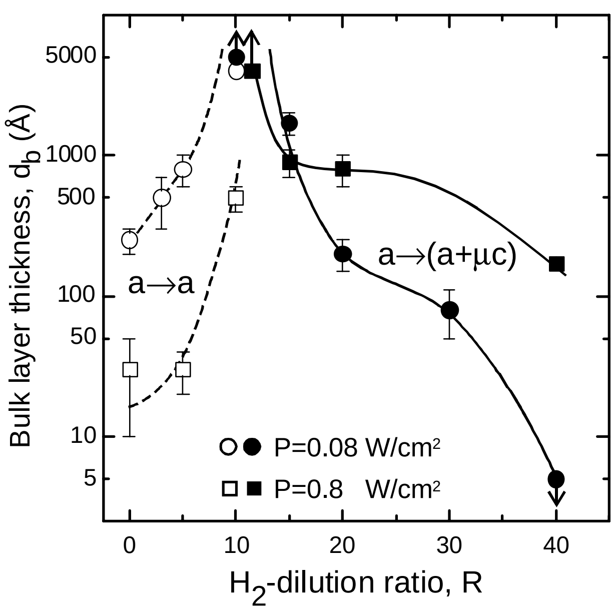

Fig. 1 A comparison of phase diagrams of rf PECVD a-Si:H i-layers under low (circles) and high (squares) plasma power conditions. The partial pressure of SiH_4 was fixed at ~0.05 Torr.

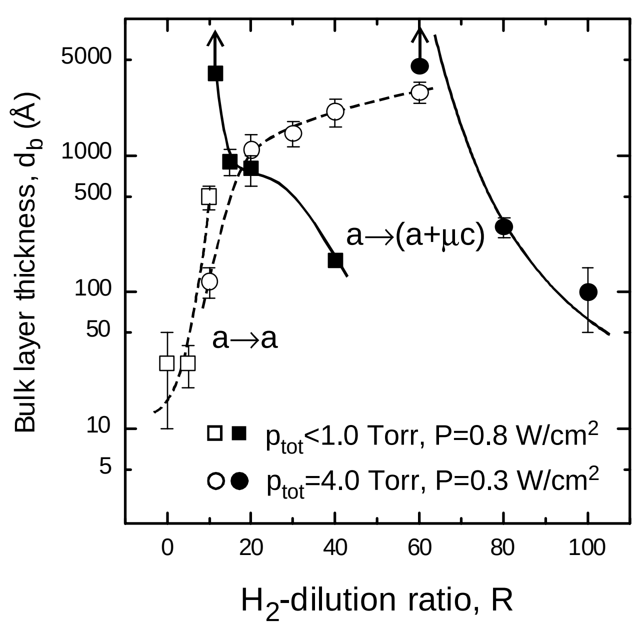

Fig. 2 A comparison of phase diagrams of rf PECVD a-Si:H i-layers under low (squares) and high (circles) gas pressure conditions. The plasma power was set to maintain similar deposition rates at the a→(a+μc) boundary (3.5 Å/s).